

Comment on “Exploring the potential energy landscape of the Thomson problem via Newton homotopies” [J. Chem. Phys. 142, 194113 (2015)]

Josep Maria Bofill^{a)}

Departament de Química Orgànica and Institut de Química Teòrica i Computacional,
 Universitat de Barcelona, (IQTCUB), Universitat de Barcelona, Martí i Franquès,
 1, 08028 Barcelona, Spain

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I. INTRODUCTION

The Potential Energy Surface (PES) and the Reaction Path (RP) are basic concepts to rationalize the chemical dynamics and chemical transformations. The stationary points (SP) of the PES are important in these concepts and it is a task for theoreticians how the SPs are connected. This is the reason why many methods have been developed in the last decades to locate SPs of index zero (minimums) and index one (saddles) (the index is the number of negative eigenvalues of the Hessian matrix) and the curves that connect these types of points. A special definition of an RP is the method of the reduced gradient following (RGF),¹⁻¹⁰ and its equivalent definition, the so-called Newton trajectory (NT).¹¹⁻¹³ For this type of RP holds that at every point of the curve the gradient of the PES points into the same direction, a direction of a prescribed \mathbf{r} -vector. The RGF is the mathematical generalization of the distinguished coordinate method.³⁻⁵

II. NEWTON: TRAJECTORIES AND HOMOTOPY

The authors of Ref. 14 use in their Eq. (3) the Newton homotopy (NH) for a potential function (PES) $V(\mathbf{x})$ with \mathbf{x} in an \mathbf{R}^N configuration space, with an additional homotopy parameter t for the $(N + 1st)$ dimension

$$\nabla_{\mathbf{x}} V(\mathbf{x}(t)) - (1 - t)\nabla V(\mathbf{a}) = 0, \quad (1)$$

here a smooth curve $\mathbf{x}(t)$ is assumed in the (\mathbf{x}, t) space. The Eq. (1) is fulfilled for $t = 0$ and $\mathbf{x} = \mathbf{a}$ which serve as the initial values. The task is to follow the assumed curve to a stationary point of V at $t = 1$.

We now execute a directional derivative in Eq. (1) with respect to t and we obtain

$$[\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})] \frac{d\mathbf{x}}{dt} = -\nabla_{\mathbf{x}} V(\mathbf{x})|_{\mathbf{x}=\mathbf{a}}. \quad (2)$$

$\frac{d\mathbf{x}}{dt}$ is the tangent of the path satisfying Eq. (1). Now, along the path

$$\frac{d}{dt} (\nabla_{\mathbf{x}} V(\mathbf{x})) = -\nabla_{\mathbf{x}} V(\mathbf{x})|_{\mathbf{x}=\mathbf{a}} \quad (3)$$

holds either if $\det(\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})) \neq 0$ or if $\det(\nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})) = 0$. At each point of the path the change of the gradient points to

the same direction, parallel to the vector $\nabla_{\mathbf{x}} V(\mathbf{x})|_{\mathbf{x}=\mathbf{a}} = \mathbf{g}(\mathbf{a})$. Thus, the direction of $\nabla_{\mathbf{x}} V = \mathbf{g}(\mathbf{x})$ does not change. Only the length of the gradient, $|\mathbf{g}|$, can change, not the direction. This behavior is inherent to the Newton trajectory (NT) or RGF curves.^{4,5,15-18} Thus any curve of a Newton homotopy of Ref. 14 may be parameterised as an NT. We note that there exists a long list of theoretical developments,^{4-7,9-13,19-30} as well as of applications of NTs in Chemistry.³¹⁻³⁸

We can, on the other hand, start with the simplest definition of an NT that the gradient lies in a fixed 1-dimensional subspace¹⁸ or that the gradient of the PES along the curve always points into a given direction:⁴ that it holds $\mathbf{g}(\mathbf{x}(t)) \parallel \mathbf{g}(\mathbf{a})$. Now t is not an extra variable, but it is only a curve parameter for the NT, $\mathbf{x}(t)$. To make the parallelism property differentiable, we norm

$$\mathbf{g}(\mathbf{x}(t))/\sqrt{\mathbf{g}(\mathbf{x}(t))^T \mathbf{g}(\mathbf{x}(t))} = \pm \mathbf{g}(\mathbf{a})/\sqrt{\mathbf{g}(\mathbf{a})^T \mathbf{g}(\mathbf{a})} = \pm \mathbf{r}, \quad (4)$$

where \mathbf{r} is now a unit vector. Thus, differentiation to t gets

$$\frac{d}{dt} \mathbf{g}(\mathbf{x}(t)) = \pm \mathbf{r} (\mathbf{g}(\mathbf{x}(t))^T \mathbf{H}(\mathbf{x}(t)) \frac{d}{dt} \mathbf{x}(t)) / \sqrt{\mathbf{g}(\mathbf{x}(t))^T \mathbf{g}(\mathbf{x}(t))}, \quad (5)$$

where $\mathbf{H}(\mathbf{x}(t)) = \nabla_{\mathbf{x}} \nabla_{\mathbf{x}}^T V(\mathbf{x})|_{\mathbf{x}=\mathbf{x}(t)}$. The treatment of the t -derivative at the singular points is described rigorously in Ref. 13 of the comment. One can insert backwards the parallelism property as follows:

$$\frac{d}{dt} \mathbf{g}(\mathbf{x}(t)) = \pm (\mathbf{r} \mathbf{r}^T) (\mathbf{H}(\mathbf{x}(t)) \frac{d}{dt} \mathbf{x}(t)) = \pm \mathbf{r} C(\mathbf{x}(t)). \quad (6)$$

$C(\mathbf{x}(t))$ is a numerical factor. Thus for the NT also holds that at each point of the path the derivation to t of the gradient points to the same direction of the vector $\nabla_{\mathbf{x}} V(\mathbf{x})|_{\mathbf{x}=\mathbf{a}}$; thus, the direction of $\nabla_{\mathbf{x}} V$ does not change. Only the length of the gradient, $|\mathbf{g}|$, can change, not the direction.

III. THE INDEX THEOREM

We can use the theory of NTs to explain properties of the Newton homotopy, for example, by using the index theorem.^{22,39} It establishes that the index changes with a difference of one along a regular NT between two different stationary points. Only if a bifurcation of the NT happens, then we are on a singular NT, then we jump to a larger index

^{a)}Electronic mail: jmbofill@ub.edu

difference, or the index retains the same value. A singular NT crosses a valley-ridge inflection (VRI) point.⁵ In the textbook of Jongen, Jonker, and Twilt,³⁹ we find the property of VRI points to build manifolds of dimension $N - 2$, if N is the dimension of the PES. Pieces of the manifold of VRI points were already often found on the PES of small molecules. A successful search is reported of VRI regions for the molecules H_2O ,³¹ H_2S , H_2Se , H_2CO ,³² C_2H_5^+ ,³⁴ HCN ,^{29,30} and H_5^- .³⁸ The approximation of asymmetric VRI points on the PES was already solved elsewhere.²⁹

The index theorem for NTs²² is coupled with the manifold character of the VRIs for Newton trajectories.⁵ The VRI manifold forms, together with the singular NTs, a partitioning of the configuration space. The situation is similar to the Mezey-partitioning of the configuration space into catchment regions for steepest descent curves.⁴⁰⁻⁴³ There the borders are formed by $(N - 1)$ -dimensional ridges starting from the SPs of index one. Regular steepest descent curves cannot cross the borders. For NTs, the borders are formed by the one-dimensional singular NTs starting at the $(N - 2)$ -dimensional manifold of VRI points. Together this set of points again forms an $(N - 1)$ -dimensional border for the partitioning of the coordinate space. Regular NTs cannot continue from one part to another. It meets a result of the commented paper¹⁴ that some trajectories do not cross a certain curve.

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